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INORGANIC COMPOUNDS AND AQUEOUS SOLUTIONS

by
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CHEMICAL EFFECTS OF IONIZING RADIATION ON SIMPLE
INORGANIC COMPOUNDS AND AQUEOUS SOLUTIONS*

By A. O. Allen

ABSTRACT

Review of existing data shows that all covalent compounds are decomposed by ionizing radiations, but that for simple molecules the reactions often will not proceed far because of back reaction of product molecules to re-form the original substances. Such systems are characterized by approach to radiation steady states, in which the various possible molecules are all present in proportions which will in general depend on the radiation intensity as well as on other variables. The concept of the constant "ion-pair yield" or "radiation yield" is valid only over restricted ranges for systems far removed from a steady state.

New experiments on the decomposition of pure liquid water are described, which show that the water decomposes to hydrogen and hydrogen peroxide or oxygen, but if these products are not continuously removed from the water a steady state is reached at very low product concentrations and decomposition ceases. Statements in the literature, apparently contradictory, on the radiation stability of water are shown to be reconciled by this scheme. The mechanism of water decomposition is discussed in detail in terms of behavior of free radicals formed by dissociation of the H_2O molecule. These radicals react readily with most solutes, and the decomposition of water by radiation is accordingly greatly affected by traces of dissolved material. Radiation effects in aqueous solutions are discussed in terms of free radical reactions. Applications to systems of biological interest are briefly indicated.

* * * * *

The effects of ionizing radiation on one type of simple inorganic compounds — namely, salts — has just been presented by Dr. Estermann. This talk will be concerned with the simple compounds which are characterized by covalent rather than ionic bonds, that is, the common gases and liquid water.

The radiation chemistry of such materials is an old field. Thanks to the excellent work of Professor Lind and his students at Minnesota, we know a great deal about the reactions produced by alpha rays in the common gases. Extensive work in this field has also been carried out in the laboratories of Professor Mund at the University of Louvain in Belgium, and contributions have appeared from other laboratories also.

Radiation sources available to these experimenters were rather weak by present day standards. Small amounts of radium or radon were used as the source of alpha rays and work was also done with X-rays from ordinary X-ray machines. With such sources only a limited proportion of the exposed material could react in any reasonable time. The experimenters naturally concentrated on measuring rates of the reactions as expressed by the ion pair yield, called M/N , which is defined as the number of molecules reacted for each ion pair formed in the reacting gas. From the values for the ion pair yield, attempts could be made to deduce the molecular mechanism of the reaction.

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With the advent of the chain reacting pile, we are faced with the necessity of exposing material to ionizing radiations for indefinite periods. The highly practical question is posed: what happens to various materials on very long exposures to radiation?

When we look over the extensive data on reactions due to radiation in simple inorganic gases, one outstanding fact appears. Almost every reaction which occurs with radiation has been shown to occur also in the opposite direction. Thus ammonia, on irradiation by alpha rays, decomposes to nitrogen and hydrogen,¹ but nitrogen and hydrogen will also react to give ammonia;² hydrogen and chlorine will react to form HCl,³ but HCl will also decompose to form hydrogen and chlorine;⁴ hydrogen and oxygen will form water,⁵ but water vapor will also decompose to hydrogen and oxygen;⁶ and similar results are found for other reactions. For every reaction occurring in radiation, there seems to be a back reaction.

One reason for the occurrence of back reactions is that the radiation will ionize all materials through which it passes. When the ions formed are neutralized, much of the ionization energy gained is given to the molecule. It is characteristic of all molecules held together by covalent bonds that the ionization energy is much greater than the bond energy. Hence, when a molecular ion is neutralized, the molecule nearly always breaks up in the reaction. Thus every covalent compound will decompose under ionizing radiation. Ionization and decomposition of product molecules will set in as soon as they are formed. In simple systems an important result will be the re-formation of the original reactant molecules.

A second way in which back reactions may occur is as a result of secondary reactions. We may start with a pure compound which is breaking up into fragments as a result of radiation. Many of these radicals combine with one another to form stable molecules not originally present. These product molecules may, however, react further with the free radicals; and the result of such a secondary reaction often is to re-form the original reactant.

In general, we may say that ionizing radiation will break all covalent bonds and the ultimate result will be that the atoms will recombine in every possible way. Thus, all possible compounds between the atoms of the system will eventually be present in greater or less concentrations. After a certain time, a steady state must obviously be reached, and no further net changes in the chemical constitution of the system will occur, as long as conditions are kept constant.

Figure 1 shows schematically how the concentrations change with increasing dosage on irradiation of simple gaseous substances. The vertical axis represents the percentage of a component of the mixture, and the horizontal axis the radiation dose, which is proportional to the number of ion pairs formed in the gas. The ion pair yield is given by the slope of the curves. Curves 1 represent a reaction in which the steady state greatly favors one compound. An example of such a substance is given by the reaction: $\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2$, where it has been found^{7,8} that if we start with pure CO_2 very little decomposition occurs and the steady state is quickly reached. If we start with a mixture of CO and oxygen, they will combine almost completely to CO_2 ; here a much longer time is required for the steady state to be reached. The ion pair yield in this case is practically constant⁸ as long as the system is far from the steady state.

Curves 2 in the diagram represent a system in which the steady state contains comparable amounts of the different compounds. An example is given by the decomposition and synthesis of hydrogen bromide.⁹ Here the system at either end is sufficiently close to the steady state so that the ion pair yield never appears to be constant; the effect of back reaction appears even very close to the start of reaction. The concept of the constant ion pair yield is, therefore, valid only over restricted ranges and for substances in which the steady state lies far removed from the initial composition of the substance studied.

The radiation chemistry of a given substance is, therefore, concerned not only with the ion pair yield for its decomposition, but also with another quantity which we may call the "radiation stability." The radiation stability of a substance may be defined as the fraction of the material remaining unaltered when the radiation steady state is reached. Thus, the literature appears to indicate that under α -ray bombardment, CO_2 is over 99 per cent stable.

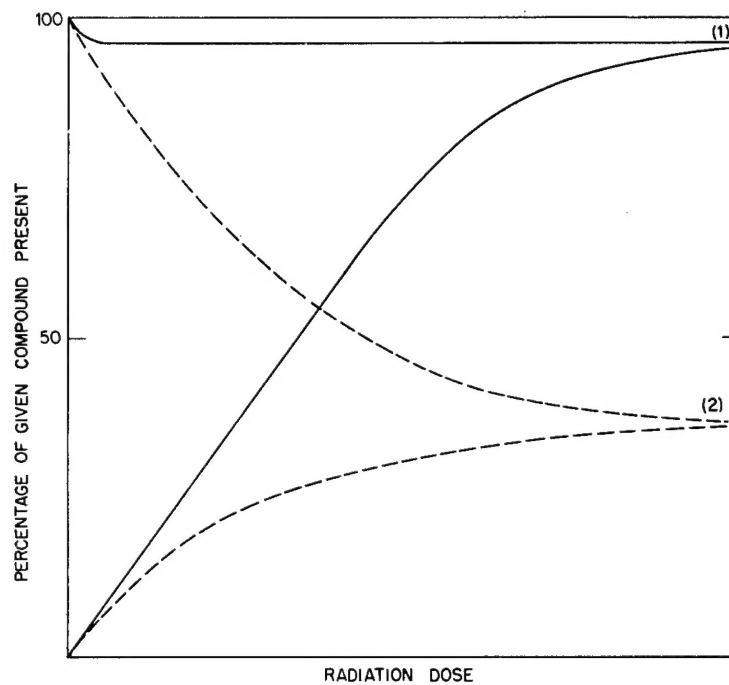


Figure 1. Results of irradiation of simple inorganic gases (schematic).

The steady state is not the same as that of thermodynamic equilibrium between the gases. Existing data suggest, however, that the most radiation stable gases are those which are also most thermodynamically stable. The reason for this is that the most thermodynamically stable gases are incapable of showing the second type of back reaction, that is, they will not react with free atoms or radicals to form other molecules. For instance, HCl gas will not react with free hydrogen atoms or chlorine atoms to form anything new, because any such reactions could be endothermic. On the other hand, both hydrogen and chlorine readily react with these free atoms to form hydrogen chloride molecules; hence, the steady state will greatly favor the HCl molecules, and HCl should possess a high degree of radiation stability.

The position of the steady state certainly depends upon the radiation intensity. This is most obvious when a molecule forms by a combination of two free radicals and may be destroyed by reaction with another free radical. The formation of such a molecule is second order in free radical concentrations and its destruction is first order with respect to free radicals. Increasing the radiation intensity increases the free radical concentrations and will favor the second-order formation reaction more than the first-order destruction reaction. The steady state concentration of the compound is, therefore, increased by high radiation intensities. An example is furnished by the appearance of hydrazine in the radiation decomposition of ammonia. Experimenters who used alpha rays to decompose ammonia found no hydrazine in the products.¹ The formation of hydrazine has, however, been noticed when ammonia is decomposed by cathode rays, which give a higher ionization intensity than the alpha sources.¹⁰ The hydrazine molecules form by the recombination of two NH_2 free radicals, and must occur in every case of radiation decomposition of ammonia; only at the higher radiation intensity is the hydrazine present in quantities great enough to be noticed.

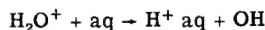
Some systems are complicated by the possibility of formation of a variety of compounds. Thus on irradiation of air, the compounds O_2 , O_3 , N_2 , N_2O , NO , N_2O_3 , N_2O_4 , N_2O_5 and perhaps others will all be

present to some extent. The experiments of Lind and Bardwell¹¹ show that the steady state in this case greatly favors the elements, oxygen and nitrogen. The radiation stability of air is therefore high, although the small amounts of nitrogen oxides found may become of practical importance in certain situations.

Mixtures of hydrogen and oxygen when irradiated may form water, hydrogen peroxide and ozone, as demonstrated by Marshall¹² with cathode rays. Duane and Scheuer⁶ long ago showed that water vapor could be decomposed by alpha rays to the extent of not more than a few per cent. Water vapor thus falls into the class of substances which are radiation stable. The situation is analogous to that of hydrogen chloride; the free atoms and radicals present will react with hydrogen and oxygen to give water but will not react with water molecules since all the possible reactions are endothermic.

Now let us leave gaseous systems, and turn to the problem of radiation effects in liquid water. What differences are expected between the effects of radiation in the liquid and the gas phase?

In the first place, the mechanism of the decomposition of the molecule is probably different. In the gas, the ion H_2O^+ is formed, which is stable and remains in this state until neutralized by a negative charge. When this neutralization occurs, much energy is given to the molecule and it will split, as with other gaseous molecules, probably chiefly to form the free radicals OH and H. In the liquid, however, it is impossible to suppose that H_2O^+ possesses any stability. Because of the high energy of hydration of H^+ the reaction

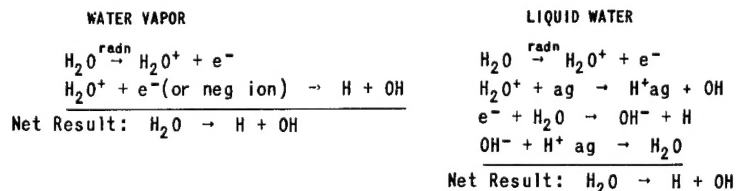


is highly exothermic, and presumably occurs immediately after the ionization act. The electron which has been set free in the ionization act likewise reacts in liquid water:



because of the high energy of hydration of the hydroxide ion. The net result, then, is again formation of H and OH radicals. Thus the end result of the primary process is the same in the liquid and gas phases, though the mechanism by which it is reached is different. (Note the diagram herewith.)

Mechanism of Decomposition of Water by Ionizing Radiations



Furthermore, the H atoms and OH radicals must react the same way in both phases, combining with each other to give H_2 and H_2O_2 ; the H_2O_2 in each case will decompose in further reactions with radicals to yield oxygen.

The important difference in the behavior of the liquid and gas is simply that when water vapor is irradiated, the products, hydrogen and oxygen, remain mixed in the reacting system and are immediately available for back reaction. When the liquid is irradiated, however, the product gases mostly escape from the liquid phase; only the small fraction which remains dissolved in the water will be subject to back reaction. This relatively small concentration of dissolved gas is, however, of great importance. It will undergo back reaction, by reason of the action on it of free radicals formed in the decomposition. The question is, what concentration of dissolved gaseous products must be obtained to reach the steady state in the radiation decomposition of liquid water? Or in other words, what pressure of gaseous products over the water is required for the steady state to be reached and decomposition to stop?

The existing literature on the radiation decomposition of water is somewhat confusing. When pure water is irradiated by X-rays, Risse¹³ reported that no decomposition occurred at all; later Fricke¹⁴ found that some hydrogen and CO₂ formed from organic impurities which were always present even in the most carefully treated water but this gas evolution stopped after a time, when all the impurities were decomposed. With alpha rays, however, Duane and Scheuer⁶ found that water was decomposed to hydrogen and oxygen at a definite reproducible rate; and their work was later completely confirmed in Lind's laboratory.^{16,15} On the face of it, this would indicate a complete qualitative difference between the effects of alpha rays and of X-rays. This seems quite unlikely, since the same processes of ionization and excitation are occurring in either case. It would seem more likely that the apparent stability of water to X-radiation should be ascribed to a steady state having been set up at so low a concentration of dissolved gases that the experimenters failed to notice it in their closed vessels.

This supposition was confirmed by some experiments performed in the Metallurgical Laboratory by John Ghormley under the author's direction. Carefully purified, degassed water was irradiated by a beam of electrons from a Van de Graaff generator. The water was placed in a bulb with a small space left for the vapor phase. A long, closed-off vertical capillary was connected to the bottom of the bulb. Initially the apparatus was evacuated and water stood in the capillary at the same level as in the bulb. When the electron beam was turned on, gas was evolved from the water in the bulb as shown by a rise of water in the capillary. The apparatus was shaken during irradiation to bring about equilibrium distribution of gas between the liquid and gas phases. As irradiation continued, the pressure on the gas continually increased by the hydrostatic head of the water in the capillary. With this small increase in pressure the rate of gas evolution decreased, and eventually stopped when the pressure had reached a value of one or two centimeters of mercury. The value of the steady-state pressure depended upon temperature, radiation intensity, and other variables. When the pressure had reached its steady-state value, it was possible by introducing some inert gas over the water in the capillary to increase the pressure on the bubble of gas in the irradiated zone. Further irradiation then caused gas to disappear. The gas would continue to disappear until its pressure was reduced to the same steady-state value as had been found before.

With this apparatus it was very simple to determine the steady-state pressure as a function of the different operating variables. Figure 2 shows the variation of steady-state pressure with radiation intensity at two temperatures. The concentration of dissolved gas at these pressures is of the order of a few micromoles per liter. (The temperature of the water was fixed by a circulating water jacket surrounding the apparatus with the exception of a thin glass window through which the electrons entered the water.) At any temperature, the steady-state pressure increases approximately but not exactly with the square root of the radiation intensity. The steady-state pressure at a given intensity decreases with a rise of temperature. This effect is to be expected since the decomposition products form by a combination of two radicals which occurs with little or no activation energy; but the destruction of decomposition products occurs by reactions between free radicals and stable molecules, which do have activation energy. Thus increasing temperature will increase the rate of destruction of the products, hydrogen and hydrogen peroxide, while having little effect on their rate of formation.

Other experiments were made using high intensity X-rays produced by the Van de Graaff generator. Careful chemical analysis of the water for dissolved hydrogen peroxide and oxygen showed steady-state concentrations comparable to those given by the electron beam. When our curve of steady-state concentration versus X-ray intensity is extrapolated to the low intensity used by Fricke, we find that he would have obtained about 0.6 micromoles per liter of decomposition products. This quantity is comparable with the amount of hydrogen which persisted in coming out of the water in his experiments after long irradiation, but which he seemed to attribute to persistence of organic impurities in the water. The equivalent amount of hydrogen peroxide which must have formed in his experiment was apparently too small to be detected by his method of analysis. We were able to measure it by a refinement of the usual iodimetric determination, in which the iodine was determined by a Beckman spectrophotometer instead of by the usual titration.

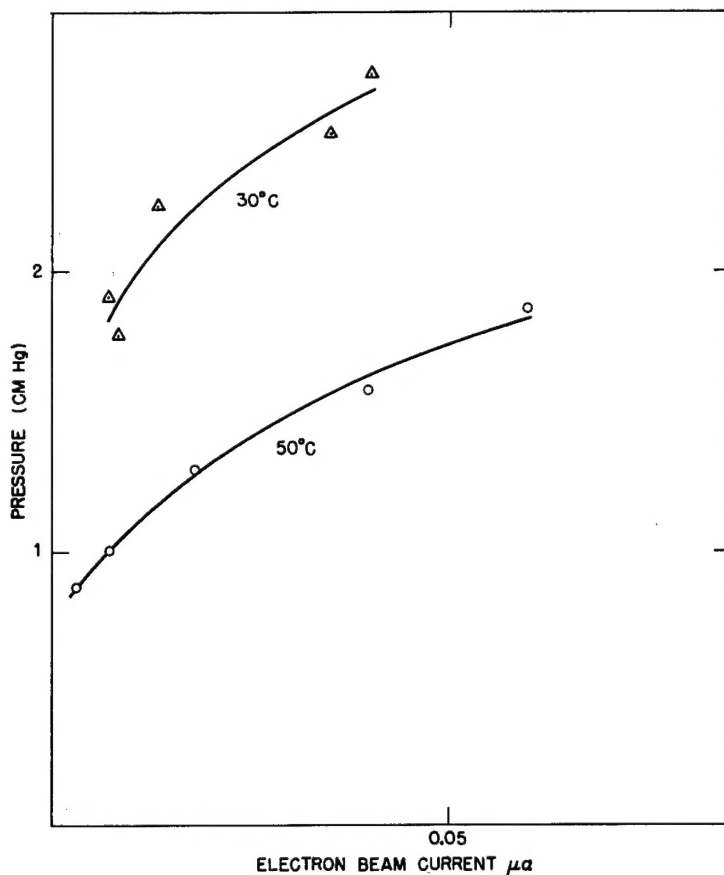


Figure 2. Steady-state gas pressure produced by bombardment of water with 1 Mev electrons.

Fricke had reported¹⁷ that a small concentration of bromide or iodide ion sensitized the decomposition of water by X-rays. Applying our gas evolution method to solutions containing $4 \times 10^{-5}M$ bromide ion, we found that the presence of the bromide caused a great increase in concentration of products at the steady state, as shown in Figure 3. We believe this effect results from a reaction between bromide ions and the free OH radicals to form bromine atoms and hydroxide ions. This reaction essentially replaces OH radicals in the solution by bromine atoms. Now it is known that in the gas phase, free OH radicals react readily with hydrogen molecules, whereas free bromine atoms do not. The effect of the bromide ions is thus to inhibit the back reaction by replacing active radicals in the solution with less active radicals. One would expect, on this basis, that the reaction products should be hydrogen and bromine; but what is actually found is hydrogen and hydrogen peroxide. The reason probably is that bromine molecules react more rapidly than hydrogen peroxide with hydrogen atoms. Thus the bromine molecules are reduced almost as rapidly as they are formed in the reaction system so that their concentration is kept at an undetectably low level, while hydrogen peroxide formed from the few OH radicals that escape reaction with bromide ions continues to increase in concentration.

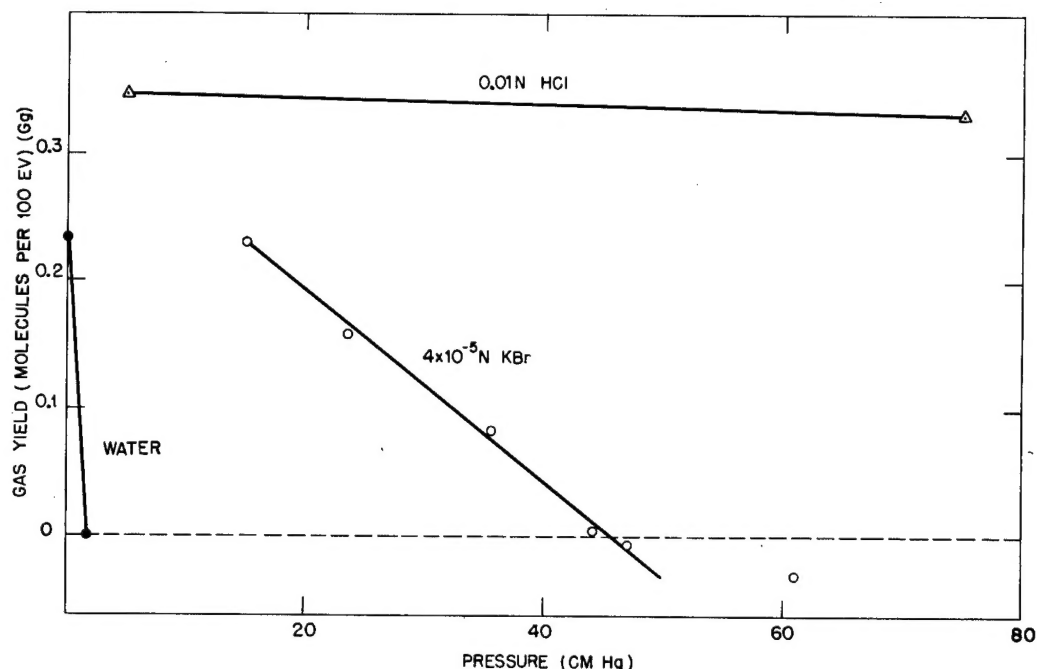


Figure 3. Gas evolution rate vs pressure for neutral bromide and acid chloride solutions.

An alternative hypothesis for the continued peroxide formation proposes that some water decomposition occurs without formation of free radicals at all. It may be that when two neighboring water molecules are both raised to excited electronic states without being actually ionized, they may sometimes react directly with each other to give $H_2 + H_2O_2$. To what extent such an ultimate molecule reaction may contribute to the decomposition of water could be told only by a thorough study of the reaction kinetics, for which our present experiments are only preliminary essays.

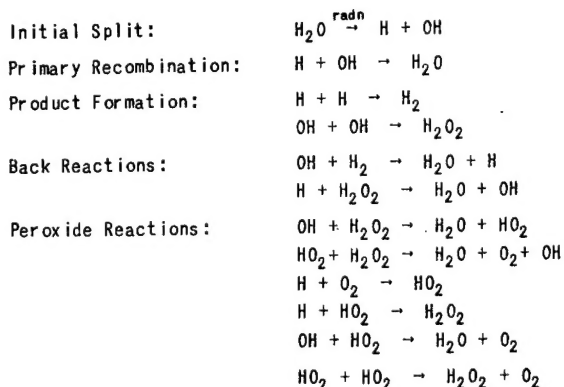
Many substances other than bromide ion will sensitize the decomposition of water. Thus we find that when pure water has stayed in the sealed apparatus for many days, higher steady pressures are found than with freshly introduced water. This effect must apparently be attributed to the accumulation of dissolved Pyrex glass in the water. The ions of the dissolved glass presumably fix the free OH into a form that will not react with hydrogen molecules—probably some sort of persilicic acid radical. Host of the oxygen acids are able to form corresponding peracids, and it accordingly is not surprising if their ions tie up the free OH radical into a less reactive form. We have found, however, that phosphate ion does not act in this way.

Fricke has reported¹⁷ that neutral chloride ion does not sensitize the decomposition of water. We find, however, that a very great sensitization occurs in solutions of 0.01N hydrochloric acid. In this solution, gas evolution occurred at a rate which diminished little with increasing pressure, indicating that the steady-state pressure must be very high (Figure 3). We have no good explanation as to why acid chloride should give a larger effect than bromide, and further study is obviously indicated.

Returning to the experiments on gas evolution from pure water, one further interesting effect was noticed. The electron beam entering the radiation cell was small and the electron penetrated only a few millimeters into the water, so that only a fraction of the water in the cell was irradiated.

It was found that when the cell was shaken during the irradiation, a much lower steady-state pressure resulted than in experiments when the cell was stationary during bombardment and was shaken only after bombardment to equilibrate the product gases between the two phases. The steady data shown in Figure 2 were obtained when the cell was shaken during bombardment. The effect of shaking is believed to have the same origin as the effect of radiation intensity. Shaking causes the free radicals to be distributed more uniformly throughout the body of water. The average radical concentration is thus lowered with resulting decrease in steady-state pressure, just as happens when the radiation intensity is lowered. The shaking effect implies that the life of the radicals is at least comparable with the period of the shaking, which was of the order of a few vibrations per second. A free radical lifetime of the order of tenths of a second seems rather large. We believe that the long-lived radical is not the reactive H or OH but rather the more stable radical HO_2 which is formed as a result of secondary reactions between hydrogen peroxide molecules and the primary free radicals.

REACTIONS OCCURRING ON IRRADIATION OF PURE WATER



This gives a list of all the reactions which must necessarily ensue from the formation of free H and OH in water. All those reactions have been demonstrated to occur freely in the gas phase and there is no reason to doubt their occurrence in liquid water also. The reactions are divided into three groups: those which produce the primary products, those which destroy these products with formation of water, thereby causing a back reaction, and those which contribute neither to the forward nor to the back reaction but are rather concerned with the conversion of hydrogen peroxide to oxygen and its reverse. The system is obviously very complicated and our present data are insufficient to determine more than the general nature of the effects occurring. Very extensive kinetic studies on pure water and simple solutions will be required to determine the details of the reaction mechanism.

To illustrate the complexities which may occur, some electron bombardments we made on 0.01N nitric acid may be mentioned. When this solution was irradiated for a short time, gas was evolved during the bombardment; but after the bombardment was stopped, more gas continued to come out of the solution, arising from a first-order thermal reaction with a half-time of about seven minutes. After the thermal reaction was over, the gas consisted of 2/3 hydrogen and 1/3 oxygen, so that the net result was the decomposition of water. By raising the pressure, gas could be made to disappear during the bombardment, as with the bromide solution; but after the bombardment gas would again be evolved. On bombarding for a long time at constant pressure, gas was evolved at a rate which gradually decreased and finally fell to zero; thus we have to deal with a steady-state volume of gas as well as a steady-state pressure. Here the initial reaction is presumably to form hydrogen gas and an unstable pernitric acid, which decomposes thermally to yield oxygen and the original nitric

acid back again. In neutral nitrate solutions, the unusual effects do not occur; the nitrate is reduced to nitrite, and oxygen is evolved as was shown many years ago by Clark and Pickett.¹⁸

The effects of radiation on aqueous solutions are a matter of great importance to those biologists who are interested in explaining irradiation effects in animal tissues. It is also a matter which arises whenever radioactive materials are dissolved in water. Many experiments on the subject are found in the literature. It is found that, in general, any oxidizable solute will be oxidized when exposed to radiation, and any reducible solute will be reduced. Organic molecules in aqueous solutions will decompose with formation of hydrogen and carbon dioxide. These effects are well recognized to result from decomposition of water to free radicals H and OH which then act on the solute molecules to reduce or oxidize them, or in the case of organic solutes, to break the bonds holding them together. The phenomenon of "protection" is a well recognized corollary of this mechanism. Dale¹⁹ and also Fricke¹⁴ have shown that if two substances are present in solution simultaneously, the more reactive material will be transformed by radiation while the less reactive substance remains inert, although the less reactive material in solution by itself would be rapidly transformed. By experiments of this kind, Dale determined the relative reactivity towards radicals in solution of a long list of different kinds of materials.

We must guard against a tendency to oversimplify this situation by forgetting or ignoring the fact that some molecular hydrogen and hydrogen peroxide will always form in the solutions. The concentration of the hydrogen may have quite an effect on the reaction of the solutes, inasmuch as the dissolved gas will compete with the solutes for reaction with oxidizing radicals. The molecular hydrogen peroxide may also enter into direct reaction with many solutes. The effective oxidizing potential of the solution is a significant quantity which will be a resultant of the concentrations of all the radicals and molecular species present. To all these complexities must be added the consideration that unstable peroxides of unusual formulas may be expected to appear frequently in the solutions. The basic idea that the action of radiation on solutions is primarily a dissociation of water to free radicals which are responsible for the reaction of the solutes is, by itself, insufficient to solve the problems of aqueous solutions. Much more extensive work is required on pure water and very simple solutions such as dilute bromide before understanding can be reached of the effects in more complicated systems. In a recent article, Weiss²⁰ has attempted to explain mathematically the kinetics of such a complicated process as the killing of bacteria by radiation in terms of simple competition of radicals for reaction with one another, or with different parts of the nucleoprotein molecules. Such theorizing would appear to be somewhat premature.

The difference between alpha- and X-radiations lies chiefly in the fact that with alpha radiation, ionization occurs with high intensity in a narrow columnar zone surrounding the actual track of the alpha particle. In between these columns very little ionization occurs. With X-rays, on the other hand, ionization is relatively uniform throughout the entire system. Thus the actual radical concentration in the active zones is always relatively high in alpha radiation even when the source of radiation itself is weak. The steady-state product concentration in water irradiated by alphas might well be expected always to correspond to a high radiation intensity. Back reactions might, therefore, become evident only at much higher pressures for alpha radiation than for X-rays of ordinary intensity. In the published experiments on irradiation of water with alphas, gas pressures were allowed to rise only to a small fraction of an atmosphere. No falling off in the yield, such as would be anticipated from back reaction, was noticed. The back reaction with alpha rays could probably be readily demonstrated by allowing the pressure of the product gases over water to rise to the order of 1 atmosphere. The yield of water decomposition by alpha rays under a pressure of 1 atmosphere of electrolytic gas should probably be considerably less than the yield at low pressures. A study of the kinetics of the back reaction in pure water under alpha irradiation, and comparison with results found with X-rays and electron beams of different intensities, should be extremely interesting.

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